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EXECUTIVE SUMMARY

PARTICULATE MATTER ANALYSIS BY ELECTRON MICROSCOPY

FINAL REPORT

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INTRODUCTION

Source apportionment estimates for particles are generally motivated either by the need to control community levels of airborne particulate matter to meet air quality standards, or by public concern over sources of local fallout. Of the two major techniques for source apportionment of particles, receptor modeling tends to be preferred over dispersion modeling.

Receptor modeling using bulk chemical analysis is a popular technique for source apportionment. The most commonly used types of receptor models are the chemical mass (or element) balance method and various types of multivariate statistical methods. The fundamental limitation of all methods using bulk analysis is that a tremendous amount of useful information is lost as a result of determining the chemical composition of the aggregates of individual particles. Thus there is a need for a receptor-based method which determines the chemistry of individual particles through the use of analytical microscopy. However, such methods are suitable for mathematical modeling only when large numbers of particles can be analyzed. This can be accomplished in a cost-effective way only by the use of an automated particle analysis (APA) system based on a computer-controlled scanning electron microscope (SEM) with an energy dispersive x-ray (EDX) spectrometer for elemental analysis. APA can be used to obtain shape, size, and elemental information about hundreds or even thousands of particles in a few days. Thus it overcomes the principal deficiency of methods using bulk chemical analysis, i.e., information about individual particles is not mixed.

The objective of this study was the development of a powerful new method for the identification of sources of airborne particulate matter, and the apportionment of the contributions of these sources to the total particle loading in community air. The method was to be based on the morphological and elemental analysis of single particles by APA, coupled with an improved method for particle classification, called Distribution Analysis, to be developed in-house.

THE DEVELOPMENT OF THE AIHL/ARB CENTER FOR AUTOMATED PARTICLE ANALYSIS (CAPA)

In basic APA methodology, particle detection is based on the strength of the scattered electron signal at each point in an SEM scan. Although previous workers have used the backscattered electron signal, the fact that most particles consisting of light elements are not detected this way prompted the development at CAPA of the use of the secondary electron signal. This required the design of new sample supports. The most useful of these was a thin carbon film suspended on a 75 mesh beryllium grid. Particles less than 1 μm in diameter could be sampled directly onto this carbon-coated grid by electrostatic precipitation. Particles larger than 1 μm could be sampled onto a carbon-coated Nuclepore polycarbonate membrane filter. After solvent clearing of the filter, the particles are left on the grid.

Initial work at CAPA centered on optimizing data acquisition from individual particles. This included the design of a new background-free carbon stub with a hole for the electron beam and a new stub holder. These improvements resulted in the acquisition of x-ray spectra free of spurious copper and zinc peaks and a continuous background reduced by a factor of 1000.

Instrument operating parameters were evaluated and a choice made of the best combination of resolution/particle detectability and x-ray signal strength/element detectability. Sample tilting, condenser lens adjustment, and instrument magnification were all factors in this optimization procedure. Magnifications of 2000x and 400x were found to be satisfactory for analyzing particles from 0.05 to 1 micron and from one to ten microns respectively. This breakdown into two size ranges is needed because of the steep falloff in the ambient particle size distribution. It also necessitates obtaining data in a region of size overlap in order to scale the data from the two size ranges together. The breadth of these size ranges represents a substantial improvement over previous work using APA, which has usually been limited to particles larger than 2.5 microns, a severe limitation considering the dominance of smaller particles in ambient air.

Because of the limited usefulness of commercially available data processing programs for source apportionment, development of Distribution Analysis, a powerful new pattern recognition technique, was initiated for implementation on the AIHL PDP-11/34 computer. The theory of Distribution Analysis was worked out with the help of Dr. Michael Tarter of U.C. Berkeley. It involves estimating source and ambient particle distributions in many dimensions: shape, size, and elemental composition. A weighted sum of source distributions is then fitted to the ambient distributions.

Use of the AIHL computer for Distribution Analysis necessitated development of programs for data transfer to the PDP. Programs were also written for sophisticated spectral processing which could more accurately determine particle elemental compositions. These routines were designed to determine a smoothed background and subtract it from elemental peak values.

APPLICATION: CEMENT PLANT

A cement plant located on the California coast was selected for initial testing of APA sampling and analytical methods because it is a distinctive, isolated source. Upwind sources are limited to marine air and a small number of automobiles. Sampling stations were located directly upwind and downwind of the plant, and representative samples of source materials were obtained from the plant itself. Air samples were collected on filters only, since problems were encountered in using electrostatic sampler in the field (these problems can be corrected). Samples were obtained on two separate days.

Source samples of coal, iron ore, laterite, shale, limestone, clinker, and cement were obtained from the plant, and used in the laboratory to generate filter samples. From the analysis of these samples by APA, particle classes were defined, i.e., source signatures were obtained.

When air samples were analyzed by APA, most of the downwind particles fell into the predetermined cement plant source classes, i.e., they were clearly plant emissions. Other particles could be attributed to windblown soil. In contrast, the upwind particles were principally of marine, sand, or soil origin, with only a small fraction being attributable to plant emissions.

This application showed that most particles can be classified by APA, and as a result those particles can be traced to their sources. However, it also revealed the chief weakness of commercial classification software, which requires the investigator to define classes of particles by inspection of analysis printouts. Distribution Analysis software will be implemented in the future to do this classification automatically even on complicated particle data sets.

PROGRESS

In its first year, progress at the AIHL/ARB Center for Automated Analysis (CAPA) has included:

Sampling and analysis techniques and substrates have been developed to allow all particles in each of two important size ranges (0.05-1 μm and 1-10 μm) to be characterized, rather than the very limited range of 2.5-10 microns previously addressable by APA.

Development of improved SEM components at CAPA have resulted in particle EDX spectra that are free of instrumental artifacts, and with a background reduced by a factor of 1000.

SEM operating parameters have been optimized to provide the best combination of particle detectability and elemental composition information.

Data processing routines have been written to transfer data to the AIHL computer, and to process elemental spectral data for greater accuracy.

Sampling and analysis of particles from one relatively simple source, a cement plant, was carried out in order to experience real world sampling problems and to test the usefulness and versatility of commercial computer programs for particle classification. This pilot study was successful in attributing most of the particles downwind of the plant to plant emissions.

FUTURE WORK

Further work needs to be done to make APA suitable for general use in source apportionment of complex mixes of ambient air particles, principally in the areas of source sampling and data processing for pattern recognition, i.e., Distribution Analysis. This work will be carried out in Phase II of the CAPA project which is currently underway. Source sampling will be applied to many sources within an airshed, and will include sampling at increasing distances from each source and simultaneous measurement of meteorological variables.

The development of data processing will concentrate on the implementation of Distribution Analysis. First attempts will assume no modification of source particles (due to fallout or adsorption of liquids or gases) for ease of computation. This analysis will then be refined by evaluation of the goodness of fit between the weighted source data and the ambient data. The residual in this fit should be interpreted in terms of missing sources as well as modification of known sources.

With these improvements in APA methodology, much more information and insight will be provided on source contributions to airborne particulate matter than has been available through more conventional bulk analysis approaches.